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PRINCIPAL  
INVESTIGATOR

James T. Kinard

NASA TECHNICAL  
OFFICER

Mr. Marion I. Kent  
DS-30  
Assistant Director, University Affairs  
NASA  
George C. Marshall Space Flight Center

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## INTRODUCTORY REMARKS

Rapid acquisition of data related to wear metal determinations in used lubricants on a regular basis and over extended periods of time is an important factor for the scientific management of vehicle performance and engine endurance. In addition, computerization of this analytical data could lead to the ascertaining of fleet trends, early detection of engine deterioration, and establishment of oil quality parameters and lubrication management programs. Such data must, however, be of high precision and good accuracy.

This investigation was launched to study the applicability of a new digestion procedure and stripping analysis to the determination of wear metals in used oil samples. This report and two manuscripts, which are being prepared for submission to the open literature for publication, culminate this research endeavor. Comments are made regarding scientific feasibility, as well as, the cost factor and analysis time for laboratory and field applications.

EVALUATION OF THE STATE OF THE ART

The initial phase of this investigation was devoted to reviewing the methods presently used in determining wear metals in used oils and evaluating the state of the art with regard to sample preparation and analytical methodology. A recent survey of the literature suggests the need for a method and procedure that will provide for rapid, simultaneous determinations of a number of wear metals, have the capability of determining concentration levels of parts per thousand to low parts per billion, require only a small amount of sample and the use of inexpensive equipment.

Original work in the 1940's involved ashing the oil and analyzing the ash. This concentrated the metals by at least one-hundred fold. Partial ashing or "coking" has also been used, which was accomplished in some instances by the dropwise addition of oil to a graphite electrode heated on a hot plate to near red heat. Most of the early work evolved around the use of spectral analysis, with a limited amount of complexometric titrations.

From the early 1960's to the present day atomic absorption spectroscopy has been employed, with a limited amount of emission spectroscopy.

Associated with these methods were a number of disadvantages, such as low efficiency in metal recover, non-applicability to simultaneous analysis, long turn-around time, expensive equipment, and poor precision or accuracy.

The employment of a new digestion procedure and anodic and cathodic stripping voltammetry provides sensitive, precise determinations of wear metals over periods of engine and lubricant use.

### FABRICATION OF ELECTRODES

The thin film mercury electrode consisted of a fresh electrochemically deposited mercury film on a wax impregnated graphite substrate. The graphite substrate was impregnated by employing a modified version of the rapid evacuation technique described by Morris and Schempf (1). The oil bath temperature was maintained at approximately 140°C and the rod was held under vacuum for a period of about five hours. Immediately following impregnation, all but one planar end of the hot rod was coated with an even layer of epoxy resin and the rod was allowed to dry in open air for five days. Prior to a series of analyses the uncoated end was polished and a film of mercury was potentiostatically plated on the freshly polished surface from 50 ml of a 0.16 mg/ml Hg (II) solution in 1.0M HNO<sub>3</sub> at a potential of - 0.200V vs. the saturated calomel electrode (SCE).

The solution was sparged for 10 minutes prior to electrolysis with purified nitrogen which had been bubbled through distilled water. Electrolysis commenced while stirring the solution magnetically for 15 minutes during film formation. The thin film mercury electrode (MFE) was held in 0.10M HNO<sub>3</sub> between series of analyses. Long periods of storage required the stripping of mercury prior to storing the electrodes in the dry.

### DESCRIPTION OF ELECTRODE ASSEMBLY AND INSTRUMENTATION

The electrochemical cell consisted of a 50 ml capacity glass bottom and a self-mounting plastic top (Princeton Applied Research Corporation, Item Numbers 9300 and 9301). The reference electrode was a saturated calomel electrode (SCE) with a salt bridge tube attached. A disk of porous Vycor (Corning Glass) silicated glass, attached at the end of the

isolated electrode tube and held in place by a Teflon (Dupont) sheath, served as the salt bridge between the isolated electrode and the solution in the electrolysis cell. The sparge tube (Princeton Applied Research Corporation, Item No. 9330) consisted of a two-way Teflon stopcock, a glass tube and a tapered Teflon tip. A study was conducted to determine the effect of adsorption due to the cell and electrode assembly on the data obtained for lead, zinc, and copper at the concentration levels and times of analysis dealt within this research. The study revealed that the effect was negligible.

A PAR 174 Polarographic Analyzer (Princeton Applied Research Corporation) in conjunction with a Houston 2000 Omnigraphic X-Y recorder (Houston Instruments) was used to obtain the anodic stripping analysis data. The instrument was operated in the direct current (dc) and differential pulse modes. The current output in the differential pulse mode represented a gain of 10, and each current is presented in this report as "true current", i.e. output divided by ten.

#### DIGESTION APPARATUS AND PROCEDURE

The digestion apparatus consisted of a Teflon (Dupont) cup and fitted cap with a stainless steel encasement. Safety specifications allowed a 0.1000 g sample of oil to be heated to 150°C in a thermostated furnace.

The warm oil samples were transported to the laboratory in 50 ml polyethylene bottles and were allowed to cool to room temperature before being weighed and digested.

Each sample was mixed thoroughly by agitation and an aliquot was weighed to the nearest 0.1 mg., then 2.5 ml of high purity nitric acid, Ultrex grade (J.T. Baker Company), was added. The cap was placed on the

cup and the cup was sealed in the stainless steel encasement. The Parr Acid Digestion Bomb (Parr Instrument Company, Moline, Illinois) was placed in a preheated furnace. After thermal equilibrium had been established the sample was heated at  $150 \pm 5^\circ\text{C}$  for a prescribed period of time. Following digestion the bomb was disassembled and the sample was transferred to a 50 ml or a 100 ml volumetric flask, and was diluted to the mark with distilled deionized water. The Teflon cup and polyethylene containers were leached with 3M nitric acid and rinsed thoroughly with distilled deionized water prior to use.

Solutions for background data were prepared by heating 2.5 ml of high purity nitric acid in the bomb under the same conditions used for the sample, and diluting to the same final volume.

#### DESCRIPTION OF PROCEDURE EMPLOYED FOR ANALYTICAL STUDY

The mercury film was deposited onto the wax impregnated graphite substrate just prior to being employed for the analytical study. For the simultaneous analysis of lead, copper, and zinc in digested oil samples a deposition potential of  $-1.10\text{V}$  vs. SCE was chosen. Reduction at this potential however, led to the evolution of copious amounts of hydrogen, suggesting therefore that further solution treatment was necessary. Addition of 4.5 ml of 5M sodium hydroxide solution to 50 ml of sample reduced the evolution of hydrogen, but this approach was abandoned for fear of forming insoluble metallic hydroxides, particularly during the stripping process when the concentration of the ions of stripped species may have readily exceeded respective solubility products at the surface of the MFE under quiescent conditions.

More suitable results were obtained by adding 2 to 3 ml of a solution of 0.5M NaCl - 2M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> to the digested oil samples and diluting each sample to 50.0 ml with distilled demineralized water. Blank solutions which had been carried through the same digestion process as the oil samples were treated accordingly.

A treated blank solution (50.0 ml) was run prior to obtaining the stripping analysis data for each digested oil sample. After five minutes of deaeration, the sparge tube was raised above the surface and the solution was stirred magnetically.

With the instrument in the differential pulse mode, deposition was initiated by placing the switch to "Ext Cell" and starting the timer simultaneously. The time of electrolysis used in this study ranged from 30 seconds to 20 minutes, unless exhaustive reduction was being conducted. After reduction, the magnetic stirrer was turned off and 30 seconds were allowed to pass before initiating the anodic scan. Since the lead concentrations in used oils were found to be much higher than the copper and zinc concentrations, zinc was stripped in the differential pulse mode up to a - 0.60V while lead was stripped with the instrument in the d.c. mode. When the potential reached -0.30V the instrument was placed on hold and the mode was changed to differential pulse. The scan was initiated again and the signal for copper was obtained.

The instrument was placed on hold again at 0.00 volt, the pen on the recorder was lifted, the cell switch was turned to the off position, and the initial potential button was depressed. The solution was then spiked with appropriate amounts of standard lead, zinc, and copper solutions and was stirred magnetically for a prescribed

period of time. The same procedure used in obtaining the signals for the sample was followed.

The area under each curve was acquired with use of a compensating polar planimeter. The background contribution was subtracted from each sample signal and spiked sample signal before calculating concentrations.

Precision studies on the simultaneous analysis of zinc, lead and copper revealed however, irregularities in the stripping data for zinc and copper for successive runs of the same sample. The stripping peak current and number of coulombs for zinc increased steadily until approaching a limiting value for consecutive runs, while the copper peak current and number of coulombs showed the reverse trend. Copeland et. al (2) noted a similar behavior and credited such to the formation a copper-zinc intermetallic that was formed in the thin mercury film during the pre-concentration step. In this laboratory, we employed scanning coulometry and chronopotentiometry to further characterize this effect, and the results appear in a separate report (3). For digested oil samples that showed a detectable concentration of zinc and copper, two approaches for analysis were taken: determination of copper selectively by potentiostatically conducting reduction at  $-0.35\text{V}$  vs. SCE for the anodic stripping analysis followed by exhaustive reduction and solution exchange, and; application of thallium as an internal standard, as described by Copeland et. al (2). While both approaches were suitable, the former was more time consuming. In addition the



MFE was suitable for the exhaustive reduction of copper for the separation process as long as the solution concentration was not high enough to lead to film saturation under the experimental conditions employed. This could lead to similar results as those obtained from attempting removal of copper by exhaustive plating on a solid electrode, that is, incomplete removal due to the disproportionation reaction between copper (II) and copper metal to form copper (I). We have found that a hanging mercury drop electrode or mercury pool was more suitable for this approach.

#### EFFICIENCY OF THE PROCEDURE

The maximum safe temperature and sample size for digesting oil in the Parr Acid Digestion Bomb are 150°C and 0.1 g, respectively. A study was conducted to determine the optimum digestion time for lead and zinc with a charge of 0.1000 g of used oil and 2.5 ml of nitric acid (70%, sp. g. 1.42). The results are shown in Table I.

Used oil samples employed in this study were dirty and contained particulate material. The sharp increase in the amount of unbound lead and zinc, when increasing the digestion time from 0.083 hour to 0.25 hour, is probably due to the leaching effect of the hot nitric acid on the particulate material, rather than any significant decomposition of metal-containing organic material. The resulting solutions at a digestion time of 0.25 hour appeared as cloudy - with small, immiscible, suspended droplets in the acid - as those at a digestion time of 0.083 hour. In addition, unused oil samples did not show an increase in the concentration of lead and zinc between these two digestion times, and organic material appeared not to be completely destroyed until at least one hour of digestion had taken place.

Solutions obtained at digestion times ranging from 0.25 to 4.5 hours showed corresponding decreasing cloudiness and increasing miscibility as the period of digestion increased. Solutions obtained after 5.0 hours of digestion were clear.

The small fluctuations in the concentration of unbound zinc for this interval of digestion times are due to experimental error, whereas the fluctuations in the lead concentration are probably due to competitive effects of the further leaching of lead from particulates and the destruction of organic material. The sharp increase in concentrations of unbound lead and zinc after 13 hours of digestion may stem from the dissolution of particulate material. However, five hours would appear to be the optimum digestion time, since it is unlikely that the inner-metal content of dirt particles stems from the wear of engines.

The efficiency of the entire procedure, including digesting, handling, diluting, and analyzing, has been determined. Standard aqueous solutions were carried through the same procedure used for digesting and analyzing oil samples. Typical results are shown in Table II for lead, since lead appeared to be the most ubiquitous of the elements studied.

The amount of lead added was the amount the Parr Acid Digestion Bomb was charged with prior to the digestion phase. The results revealed that even for extended digestion periods, loss due to volatilization is insignificant. In addition, the effects of contamination or loss due to sample transfer, adsorption and desorption, etc. are insignificant.

Table I      Digestion Time Versus Concentration of Unbound Lead  
and Zinc in a Used Oil Sample

<u>Digestion Time</u> <u>Hours</u>	<u>Concentration of Metal</u>	
	Lead	Zinc
	parts per thousand	parts per billion
0.08	12.0	3.38
0.25	26.8	3.66
0.50	25.6	3.54
1.0	27.5	2.46
2.5	21.2	3.58
3.0	18.2	3.45
4.5	20.9	3.34
5.0	22.0	3.73
7.0	23.4	3.73
11.	25.0	3.73
13.	30.7	4.80

Table II                      Efficiency of the Entire Procedure for Lead \*

<u>Time of Digestion Hours</u>	<u>Amount of Lead Added <math>\mu\text{g}</math> /ml</u>	<u>Amount of Lead Found <math>\mu\text{g}</math> /ml</u>	<u>Percent Recovery</u>
5	9.51	9.63	101
5	9.51	9.53	100
13	9.51	9.82	103

Mean = 102.

Standard Deviation 1.85%

\* Data reflect the combined effect of the digestion process, the transfer and dilution of the sample, and the analytical determination by anodic stripping analysis from the MFE.

## CONCLUSIONS

The use of the PARR ACID DIGESTION BOMB and the employment of anodic stripping analysis constitute a means for the rapid, precise evaluation of wear copper, zinc, and lead in used oils. The mercury film on a wax impregnated graphite substrate is a rugged electrode system that is particularly suitable for field work. It provides for the detection of concentrations as low as  $10^{-11}\text{M}$ , and as high as  $10^{-6}\text{M}$ , thereby making it suitable for the evaluation of minute or critical variations in engine deterioration.

After fabrication of the electrode a typical analysis can be performed (using the internal standard method) from 3 to 12 minutes. Thus, over an eight hour period from 40 to 160 samples can be analyzed, depending upon the concentration range of wear metals investigated. Samples can be digested far in advance of analysis and can be easily transported in the Teflon cups without fear of contamination. In addition, use of the Teflon cup as the cell bottom reduces the time of sample preparation by about five minutes, and the chance of contamination.

Instrumentation can be purchased or constructed at a very modest cost (\$4000.)

REFERENCES

1. Morris, Joseph B. and Schempf, John M., Anal. Chem. 31, 286(1959).
2. Copeland, T.R., Osteryoung, R.A., and Skogerboe, R.K., Anal. Chem. 46, 2093 (1974).
3. Manuscript is presently being typed and will be ready for submission to be considered for publication by February 15, 1975.